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Solidification of Radioactive Organic Liquid Waste

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Abstract

As a byproduct of nuclear generation operations, Ontario Hydro produces small volumes of radioactive organic liquid wastes such as contaminated hydraulic oil, Freon sludge from dry cleaning operations and the liquid effluent from compaction operations. In addition to low levels of fission (Cs-137, Cs-134, Ru-106) and activation (Co-60) products, these wastes were found to contain variable amounts of halogenated species, polychlorinated biphenyls and tritium which may make solidification preferable to incineration.

Waste loadings of approximately 55% waste oil or supercompactor effluent were achieved by preabsorbing the waste on swellable polymer particles followed by encapsulation in an epoxy-modified Portland cement binder. The effects of detergent on the curing of Portland cement limited Freon sludge waste loadings to less than 40% by volume. Waste loadings could be increased by approximately 10% if aqueous decontamination wastes were used as the hydration water. Commercially available solidification agents, such as Environstone gypsum, Nutek and Petroset II generally provided lower waste loadings and exhibited either poorer oil retention or mechanical integrity.

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SOLIDIFICATION OF RADIOACTIVE ORGANIC LIQUID WASTE

1.0 INTRODUCTION

The Ontario Hydro license to store radioactive waste at the Bruce Waste Operations Site does not allow storage of liquid waste and presently the bulk of low level radioactive organic liquid waste is stored at the generating station sites. Thus there is a need to develop a strategy to treat and store or dispose of these wastes. Incineration is both the most efficient and the preferred method of low level waste treatment. However, immobilization may be a requirement for the transportation of liquid wastes and may also be necessary for waste treatment during incinerator outages or where the liquid wastes cannot be incinerated due to high halogen, radionuclide or toxic chemical content. Immobilization can be achieved either through absorption of the liquid waste onto a solid to prevent dispersion, or by using a binder to solidify the liquid waste as a monolithic solid wasteform. Pursuit of either absorption or solidification will depend on the relative advantages of the final wasteform viz. cost, waste capacity, physical integrity, requirements for repackaging for disposal. Absorption of liquid waste is being studied as a continuation of this research and will be reported separately.

In the case of aqueous wastes there are many successfully demonstrated techniques for treatment of which the water extendible polyester prototype plant which was recently commissioned is one/1/. However, there are organic waste streams generated by Ontario Hydro's nuclear stations which are generally incompatible with aqueous waste solidification techniques, such as water-extendible polyester (WEP) or Portland cement. Since incineration may not be economical for the small volumes foreseen and because an incineration facility may not be available in the future, an immobilization strategy is desirable to comply with the operating license.

There are three streams which have been identified as composing the bulk of organic radioactive waste at Ontario Hydro (see Table 1)/2/. Spent lubricating oil is by far the largest of the three in terms of storage inventory. However, Freon sludge from dry cleaning operations and effluent from proposed supercompacting operations will eventually account for a relatively large proportion of the waste.

Table 1

Radioactive Organic Liquid Waste
Arising at Ontario Hydro

Waste	Accumulated Volume m^3	Future Generation Rate m^3/yr
Contaminated Lubricating Oil	194	6
Freon Sludge	4	9
Supercompactor Effluent	-	6

Source: Reference 1

This study was divided into two parts, characterization of the likely waste streams and solidification studies, with the objective of developing a single solidification system for all three waste streams. The solidification work was further divided between active and inactive investigations. Where possible, inactive analogs of the wastes were used but in the case of Freon sludge and supercompactor effluent the heterogeneous nature of the waste made the development of inactive analogs impossible. After the most successful techniques had been selected from the results of the inactive tests the compatibility with active wastes was tested.

2.0 EXPERIMENTAL

2.1 WASTE STREAM CHARACTERIZATION

Waste stream samples were obtained as follows. Contaminated fuelling machine oil is stored at the generating stations in drums and may be contaminated with solvents, water and various other organic waste. Two samples were obtained, one was a composite of several samples from the bottom of five separate drums and the other was a composite of samples from the centre of 20 separate drums.

Freon sludge samples were produced by distilling the Freon waste taken from dry cleaning machines at BNPD-CMF to a level comparable to that achieved by a typical Freon distillation recovery (final temperature=95C)/3/.

The supercompactor effluent sample was obtained from a demonstration run of a Westinghouse supercompactor using as waste feed empty heavy water drums along with assorted non-processible waste and compactible trash at BNPD Radioactive Waste Operations Site (August, 1986).

Representative portions of each waste stream were tested for pH and density. The water content was determined by Karl Fischer titration, the halogen content by neutron activation analysis and gas chromatography (electron capture detector) was used to measure the concentrations of PCB's and Fyrquel. Gamma spectrometry and liquid scintillation counting (C-14, H-3) were employed to determine radionuclide activities. A solids determination was performed by filtration.

2.2 SOLIDIFICATION STUDIES

2.2.1 Wasteform Criteria

In the absence of any Canadian criteria for low level radioactive liquid waste solidification, several experimental criteria were derived for the purpose of wasteform comparison.

i) Formation of a stable, workable mixture.
ii) High waste loading (% by volume) which will reduce considerably the cost of both storage and solidification media.
iii) Minimal or no waste pretreatment.
iv) No free liquid after curing and as little as possible waste release after 90 days immersion in water.
v) A compressive strength exceeding 0.35 MPa to facilitate shallow burial or stacking in storage facilities/4/.

2.2.2 Wasteform Testing

The testing program was divided into two components:

i) Tests using inactive analogs of the wastes to determine the optimum binder matrix. Test specimens were produced using various formulations incorporating Portland cement, plaster of Paris, limestone-injected fly ash, epoxy resin, and numerous additives. Terresso 32 turbine oil or its equivalent was used as an analog for the lubricating oil waste. Because of the heterogeneous nature of the Freon sludge and supercompactor effluent no inactive analogs could be produced and thus the inactive tests were restricted to inactive lubricating oil.

ii) Tests using radioactive Freon sludge and supercompactor fluid to optimize the best binder from i) above for these wastes.

For part (i) there were two phases to the testing procedure. In the initial phase, test specimens were prepared in 500 mL polyethylene jars (according to the procedure in Appendix A) for a cursory screening procedure. After a seven day cure, direct thumb pressure (measured to be approximately 0.35-0.4 MPa) was applied to ensure adequate compressive strength. The jar was subsequently filled with water and the quantity of released oil (measured as % by volume of original waste oil) estimated after 3 day and 14 day intervals. In the second phase a number of the more

successful wasteform compositions were reproduced and allowed to cure for 28 days in 5x5x5 cm cubic molds. Three of these were tested for compressive strength immediately and the remaining three tested after immersion in 1200 mL of water for 90 days.

In addition to those solidification binders listed in part (i) above, unsaturated polyester (WEP) was also considered. However, the development of a WEP process for waste oil immobilization constitutes a complete research project in itself and will be reported separately.

3.0 DISCUSSION

3.1 WASTE CHARACTERIZATION

In order to facilitate selection of a waste management option, characterization of the waste streams was performed. The results are presented in Table 2. Of the three wastes listed, only the PNGS lubricating oil is suitable for incineration. The Freon sludge contains both too much suspended solid matter and too large a halogen content. The former may result in plugged injection lines or burners and the latter raises the problem of acid gas (HCl and HF) corrosion. It is expected that future dry-cleaning fluid recovery will yield sludge containing a more acceptable halogen concentration of approximately 1600 μg/g and that absorption on a combustible solid waste will avoid problems with the plugging of liquid injection burners. The supercompactor effluent also has a high solids content in addition to a PCB concentration above the limit for incinerable material (50 ug/g) and a relatively high level of tritium. Since the composition of this last waste stream depends on the feed to the compactor, which is expected to be extremely variable, there could be other reasons not to incinerate the effluent. As was suggested elsewhere for Freon sludge/5/, supercompactor effluent could be rendered incinerable if sufficient "clean" and absorbent solid waste were available as a carrier. In the event that such a resource is unavailable or that the necessary waste handling is undesirable, solidification must be considered. This is particularly true when the concentrations of undesirable components are expected to be so variable.

It is interesting to note that, as expected from the greater density, the PNGS oil 'bottoms' sample has higher concentrations than the oil 'centres' for water, solids, tritium and both fission (Cs) and activation (Co) products. The halogen concentration is higher in the 'centres' sample indicating a halogenated hydrocarbon form rather than a dissolved or crystallized salt. Because of the difference in oil sample origin (5 drums versus 20 for the centres sample) it is not possible to make more detailed comparisons such as the ratio of water to tritium. However, Table 2 does provide an approximate estimate of the expected waste stream composition.

Table 2

Characterization of Miscellaneous Liquid Wastes

	PNGS Oil "Bottoms"	PNGS Oil "Centres"	Freon Sludge	Supercompactor Effluent
Density g/mL	0.87	0.86	1.01	0.88
Water Content g/kg	12.5	2.7	44	860
pH	6.8	6.8	5.0	8.1
Suspended Solids g/L	0.17	0.1	5-Unfilterable	Unfilterable
Halogens µg/g	66	1233	~35000[1]	280/380/440(Cl)[2]
PCB µg/g	<5	<5	-	130[3]
Fyrquel µg/g	<5	<5	-	440[3]
Tritium mCi/L	2.5	0.13	0.002	210
Carbon-14 mCi/L	<0.06	<0.06	<0.06	<0.06
Cs-134 nCi/L	3.1	0.3	21	350
Cs-137 nCi/L	56	2	94	6200
Co-60 Ci/L	260	6.5	37	1030
Ru-106 nCi/L	-	-	-	370
Balance of sample	Heterogeneous mixed organic phase (primarily hydrocarbon oil)			

1 Taken from reference 3.
2 Oil/aqueous/sediment phase, respectively.
3 Oil phase only.

3.2 SOLIDIFICATION MATRIX FORMULATION - INACTIVE OIL RESULTS

Solidification usually depends on the dispersal of the hydrophobic waste in a hydrophilic binder such as Portland cement, gypsum (hydrated plaster of Paris) or a polymeric binder such as epoxy or polyester. In the present study a number of different binders were tested such as plaster of Paris, Portland cement and epoxy resin. To compensate for the various undesirable characteristics of each binder a number of additives were employed including emulsifiers to disperse organic waste in the hydrophilic binders, waterproofing agents to reduce porosity, fillers to reduce cost, cement hydration accelerators and absorbents to reduce both waste displacement and interference with solidification reactions.

3.2.1 Portland Cement

Hydraulic cement is the most widely employed solidification binder for radioactive liquid waste, because of its low cost, good compressive strength and ease of use. In a previously reported study Portland Type 30 (PC) was preferred over high alumina cement (HAC) because of its tolerance to alkaline solutions, lower volume increase and often faster setting time /6/. The high aluminate concentration of HAC would be a liability in solidifying organic waste since organic materials solubilize the aluminates and the resulting gel hinders proper hydration and setting of the cement. The major disadvantages of PC are its hydrophilic character and open pore structure: the organic waste is not chemically bound with hydrophilic PC and an open pore structure allows displacement of the waste due to hydrostatic forces when the sample is immersed. However, these difficulties can be mitigated by the use of absorbents, emulsifying agents and waterproofing agents.

a) The Effect of Emulsifier Addition: In Table 3 are presented specimen formulations with varying amounts and type of emulsifiers. The rate and amount of oil release after immersion will depend on the size of the cement pores which contain oil. The pore size in turn depends on the efficiency of dispersal of the organic into fine droplets. Large amounts of emulsifier facilitate more efficient dispersal (sample A26, Table 3). Nonionic emulsifiers appeared to be more efficient and had a lesser effect on cement setting than either anionic or cationic emulsifiers. Of these three nonionics listed, Swift Solar F342 appears to have been the most effective. All of the wasteforms have sufficient strength although the actual compressive strength is probably greater for the sample with the smallest pore size.

b) Polymeric Additives: Polymers are often added to Portland cement to waterproof the product. The polymer fills the pores and cures, thus reducing porosity. In Table 4 are presented test results from cement wasteforms with added acrylic resin suspension or epoxy resin. Increasing amounts of acrylic suspension improved the oil retention properties of the wasteform. Although sample A24 contained 15% (40 mL) acrylic suspension (mostly water), there was no further reduction in oil release thus indicating that the optimum proportion lies between 5 and 15% acrylic by

Table 3

Effect of Emulsifier Type and
Concentration on Waste Form Performance

Specimen	A9	A25	A19	A22	A26
Emulsifier mL	13	13	13	6.5	26
Type	X-100	Solar F342	X-114	X-114	X-114
Oil mL	130	130	130	130	130
PC g	170	170	170	170	170
Water mL	50	50	50	50	50
Acrylic Suspension g	10	10	10	10	10
Waste Loading (% Vol)*	46	47	45	47	38
Compressive Strength >0.35 MPa	Yes	Yes	Yes	Yes	Yes
Oil Release (%)					
After 3d	7-12	<<1	1-3	1-3	1-3
14d	31	1.5	3	6	2

Table 4

Waterproofing Additives in Portland Cement

Specimen	A9	A15	A16	A24	E2
Epoxy g	-	-	-	-	40
Acrylic g	10	15	20	40	-
Oil mL	130	130	130	130	130
PC g	170	170	170	170	170
Water mL	50	45	40	20	50
Emulsifier mL	13	13	13	13	13
Waste Loading (% Vol)*	46	48	47	44	46
Compressive Strength >0.35 MPa	Yes	Yes	Yes	Yes	Yes
Oil Release (%)					
After 3d	7-12	1-3	<1	1-3	<1
14d	31	11	4	7	<1

* $\frac{\text{Oil Volume}}{\text{Volume of final waste form}} \times 100\%$

volume of the wasteform. Epoxy resin was a more efficient waterproofing agent since the amount of oil displaced by water is much less in sample E2 than in any of the acrylic-containing samples. No optimization of the proportion of epoxy was performed since the ratio of cement and epoxy used here was determined in a previous study/7/ to provide the best combination of compressive strength, workability of the mixture and water resistance of the wasteform.

c) Mineral Additives: Coal flyash has been added to Portland cement to reduce its cost, improve workability and reduce excess water requirement (thus reducing porosity). Limestone-injected flyash (LIF) further adds free lime and calcium sulphate to the mix, providing either reduced setting times or further reducing the PC requirement.

From Table 5 it can be seen that complete replacement of the Portland cement by LIF or plaster of Paris results in compressible and therefore unacceptable products. However, use of up to 50% plaster of Paris, LIF or flyash can reduce binder cost and appears to actually improve oil retention during immersion testing.

Table 5

The Effect of Binder Substituents on Wasteform Performance

Specimen	A9	A14	B3	B4[1]	C4	C2
Flyash g	-	85	-	-	-	-
LIF g	-	-	85	170	-	-
Plaster of Paris g	-	-	-	-	85	170
Acrylic Suspension mL	10	10	10	10	10	10
Oil mL	130	130	130	130	130	130
PC g	170	85	85	-	85	
Water mL	50	50	50	50	50	50
Emulsifier mL	13	13	13	13	13	13
Waste Loading (% Vol)	46	47	47	46	48	46
Compressive Strength >0.35 MPa	Yes	Yes	Yes	No	Yes	No
Oil Release (%)						
After 3d	7-12	1-3	<1	1-3	<1	<<1
14d	31	1	<1	10[1]	1	1

1 Wasteform cracked and deteriorated after 3 days.

d) Absorbents: Organic waste can not only retard the setting of cement but, because of the open pore structure of hydrated cement and the lack of a chemical bond between the cement and the waste, can also be easily

displaced by hydrostatic pressure when the sample is immersed in water. Use of a hydrophobic absorbent would sequester the organic fraction and reduce these effects. A granular absorbent would be required to facilitate mixing of the binder and waste. DOW imbiber beads, hydrophobic crosslinked alkylstyrene beads (diameter <1mm) which can absorb up to 27 times their volume of oil, were selected as the best absorbent from a list described in an earlier report/8/.

The effects of oil/bead ratio and premixing time (prior to incorporation into the cement mixture) on the oil release characteristics of the waste can be seen in Table 6. A comparison of samples IB2, T14 and T15 indicates that despite the higher waste loading in samples T14 and T15, an oil/bead ratio of 5 reduces the amount of oil released in the immersion test. Oil release data from samples A9, IB9 and IB14 illustrate the improvement afforded by adding imbiber beads to absorb the oil and, better yet, by imbiber beads premixed with the oil waste. Sample sets IB9/IB14, IB2/IB10/IB8 and T15/T14 show more clearly the reduction in oil release with increasing periods of oil and bead premixing. Obviously, smaller amounts of free oil result in better oil retention and both a lower oil/bead ratio and longer absorption times reduce the volume of free oil. Finally a comparison of sample pairs IB2/IB9 and IB14/IB10 indicates that, as expected, a combination of imbiber beads and a waterproofing agent works better than either additive alone (see also Table 7).

Because the oil-swollen beads are relatively large and non-deformable, they do not require large amounts of emulsifier in the formula to maintain a dispersed state. Thus specimens T14, T15 and later test products, which also have an oil/bead ratio of 5, contain little or no emulsifier.

e) Extended Wasteform Tests: Based on the foregoing results and discussion, several of the best test specimens were selected for the extended second phase testing. Several new wasteforms were prepared using both absorbents and waterproofing agents. In Table 7 are presented the results of this more extensive test program. Samples A9 and IB8 were discussed previously. Samples E12 and T12 were developed by adding acrylic suspension and epoxy resin waterproofing agents to sample IB8 to further reduce oil release. Samples C4a and C4b are analogous to samples A9 and IB8 except that half of the Portland cement has been replaced with plaster of Paris (see part (c)).

The sample which best meets the criteria set forth in Section 2.2.1 is E12 since it exhibits a relatively high wasteloading of 54%, more than acceptable compressive strength and excellent oil retention after immersion in water for 90 days. Waste loadings in this waste formulation have been successfully increased to 60% without deterioration in the product performance. Sample T12 and sample C4b also showed reasonable oil

Table 6

Effect of Absorbent on Wasteform Performance

Specimen	A9	IB9	IB14	IB1	IB2	IB10	IB8	T15	T14
Imbiber beads mL	-	13	13	4	13	13	13	20	20
Mixing time (hrs)	-	-	2	-	-	2	6	7	20
Oil mL	130	130	130	130	130	130	130	100	100
Oil/Bead ratio	-	10	10	33	10	10	10	5	5
Cement g	170	170	170	240	230	170	170	100	100
Water mL	50	50	50	100	100	50	50	50	50
Emulsifier mL	13	13	13	13	13	13	13	2	2
Acrylic Suspension mL	10	10	10	-	-	-	-	-	
Waste Loading (% Vol)	46	46	47	47	47	47	47	50	50
Compressive Strength >0.35 MPa	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Oil Release (%)									
After 3d	7-12	1-2	<1	7-12	7-12	<1	<1	<1	<<1
14d	31	5	<1	-	-	3	1.5	3	<<1

Table 7

Wasteform Characteristics of Various Solidification Systems

Specimen	A9	IB8	E12	T12	C4a	C4b
Binder	Portland Cement	Portland Cement	Portland Cement	Portland Cement	Portland Cement/ Plaster of Paris	Portland Cement/ Plaster of Paris
Additives Imbiber Beads/Oil ratio	-	5:1	5:1	5:1	-	5:1
Acrylic Suspension (%)	3.5	-	-	25	3.7	4.4
Epoxy Resin (%)	-	-	8.6	-	-	-
Emulsifier (%)	4.6	4.7	-	-	4.8	4.8
Waste Loading (% Vol)	46	47	54	50	48	48
Compressive Strength (MPa)						
- Before Immersion	1.9	1.8	1.2	1.9	0.44	0.33
- After 90 d Immersion in Water	3.4	3.8	1.5	2.9	0.57	0.54
Fractional Oil Release After Immersion, 90 d	0.32	0.01-0.02	<0.01	0.01	0.13	<0.01

retention at a slightly lower wasteloading but the compressive strength of specimen C4b is marginal and sample T12 exhibited both a sticky surface covered with easily removable oil-swollen beads and slightly poorer oil retention after immersion in water.

3.2.2 Epoxy as a Binder

The use of a waterproof thermoset resin, such as epoxy, as a binder would remove all concerns about compressive strength and oil retention. However, epoxy is neither oleophilic nor hydrophilic and the dispersion of the waste in the binder becomes a problem. Attempts to produce an organic waste-in-epoxy emulsion using a filled epoxy (Sikadur) ended in failure. The product (sample SC3 in Table 8) had an open pore structure due to the large amount of organic waste used (and agglomeration of the oil phase) and acted like a sponge, desorbing when compressed and absorbing when compression was released. The use of imbiber beads to absorb the oil, prior to mechanical dispersion of the beads in the epoxy binder met with some success. Samples EC2 and EC6 exhibit relatively high waste loadings (50-60%) and excellent oil retention characteristics: virtually no oil was observed in the immersion water after 90 days. Both of these samples use a water-tolerant epoxy, Epon 815, with the 501 hardener. A test specimen prepared with Sikadur epoxy and imbiber beads (sample SC1) exhibited oil release from the dry product. Oil appeared to ooze from the oil-swollen beads on the surface of the wasteform.

Because of the relatively high cost of epoxy resins it is customary to use a nonreactive, finely divided mineral filler. Calcium carbonate was used here but flyash was also found to be acceptable. Sikadur epoxy had the gritty texture of a filled epoxy and so the amount of filler used with this resin was less than for the Epon resin.

For the solidification of mixed organic and aqueous wastes in epoxy resin, it would be necessary to use a material capable of absorbing both phases, such as sawdust. This idea was not pursued further since an epoxy binder exhibits few significant advantages over epoxy-modified Portland cement which justify the increased cost.

3.3 COMPARISON WITH COMMERCIALLY AVAILABLE SOLIDIFICATION SYSTEMS

As noted previously, there are several liquid waste solidification systems which are available commercially and some of these are capable of solidifying oil. The characteristics and performance of three of these are presented in Table 9.

The Nutek system relies on a proprietary emulsifier to render the oil compatible with a Portland cement (PC) binder. Added lime and a proprietary accelerator are utilized to ensure setting of the product. The result is a hard but porous wasteform that releases considerable oil (13% to 33%) when immersed in water.

Table 8

Wasteforms Using An Epoxy Binder

Specimen	EC2	EC6	SC1	SC3
Imbiber Beads (g)	20	20	20	-
Waste Oil (mL)	100	100	100	100
Epoxy (g)	60	40	60	48
Filler ($CaCO_3$)(g)	30	20	20	40
Wasteloading (% Vol)	55	62	65	50
Compressive Strength >0.35 MPa	Yes	Yes	Yes	No
Oil Release (%) After 14 d	<<1	<<1	oozes oil	([1])

([1]) Acts like a sponge.

Table 9

Wasteform Characteristics for Commercially Available Solidification Systems

Specimen	Nutek	Envirostone	Petroset II
Binder	Portland Cement/ Lime (10%)	Gypsum/ Proprietary Polymer	Proprietary
Additives:			
Emulsifier Type(%)	380A/Proprietary (25)	Proprietary (4.2)	-
Accelerator Type(%)	380B/Proprietary (3.3)	-	-
Other	-	Proprietary Polymer	Methanol (5%)
Waste Loading(% Vol)	40	42	73
Compressive Strength (MPa):			
Before Immersion	6.5	-	Not a solid (stiff gel)
After 90 Day Immersion	9.4	1.4	Unchanged
Oil Release After 90 Day Immersion in Water (%)	13-33	13	<<1

Envirostone solidification also relies on an emulsifier and has reduced setting problems because gypsum is used as the binder instead of PC. A polymer additive is also included, presumably to improve compressive strength and reduce permeability to water. Nevertheless the product is much softer than the Nutek product (although still harder than 0.35 MPa) and loses 13% of the solidified oil during immersion. It is interesting to note that the Plaster of Paris/PC composite described in Table 7 performed as well as the Envirostone gypsum except in compressive strength, possibly due to the higher waste loading of the former. Both Nutek and Envirostone allow moderate waste loadings (~40%) on the advice of their manufacturer, higher loadings would probably result in free oil or would prevent the wasteform from setting.

The third product, Petroset II, consists of a proprietary powder, possibly a colloidal gum, which is mixed with the waste oil and activated by a lower alcohol such as methanol. The resulting stiff gel had a high waste loading, released no oil during immersion but was deformable. When this product was added to PC paste in an attempt to improve the compressive strength of the product, copious amounts of oil were released during immersion in water. No tests were performed to ascertain long term product stability.

None of the commercial systems fulfill all of the criteria set forth in the introduction to this report. Neither the Nutek nor the Envirostone products retain the oil to a sufficient degree when immersed. The best of the developed matrices (E12) released less oil and had a higher waste loading than either Nutek or Envirostone. Only the Petroset II product had a higher waste loading than E12 although a rigid container would be required to offset the lack of compressive strength. If such a container were available the high waste loading, excellent oil retention and ease of incineration of the Petroset material would be advantageous.

3.4 CO-SOLIDIFICATION OF ORGANIC AND AQUEOUS LIQUID WASTE

All of the solidification media discussed above, with the exception of epoxy resin, require hydration water which can be replaced with spent aqueous decontamination solutions, thus increasing the waste-loading of the final product. In a previous study/6/ of the cementation of various decontamination wastes, a waste loading of up to 29% by weight could be achieved in Portland cement.

The hydration water was replaced by decontamination solutions, including Turco 4521A, Calgon, Nacconal, Pickering solution, sodium tripolyphosphate, peroxide bicarbonate and alkaline permanganate, in formulation E12. Except for Turco 4521A, which requires pH adjustment, all samples cured in a satisfactory manner yielding hard products which released less than 1% of the organic waste after immersion in water for 14 days. The order of increasing oil release was Nacconal<alkaline permanganate<Calgon and Pickering solution<peroxide bicarbonate. The specimen containing Turco 4521A did not harden at all and exhibited a strong odour of ammonia. Untreated electolyzer solution (25% KOH), used at the Tritium Removal Facility to promote electrolysis of tritiated heavy water, was also

solidified but resulted in a compressible product.

With one exception, that of alkaline permanganate, these findings are consistent with those found in the previous work thus indicating a lack of chemical interaction between the decontamination solutions and formulation E12. The lack of previous success in solidifying untreated alkaline permanganate solution probably stems from the higher waste loading used in that study. Larger quantities of aqueous waste can be solidified at the cost of a lower organic waste loading, however the consequent increase in the porosity of the cement would probably result in an increase in oil release and require more of the relatively expensive epoxy resin for waterproofing purposes. The final waste loading achieved generally equalled 10% aqueous waste and 50-55% organic waste. It is expected that the results of co-solidification with supercompactor effluent will be similar to those reported above for oil. However due to the retarding effect of detergents on the curing of cement, detergent-containing wastes such as Calgon, Nacconal, Pickering solution and STPP are not recommended for co-solidification with Freon sludge, which already contains a detergent.

3.5 SOLIDIFICATION OF ACTIVE WASTES

3.5.1 Solidification of Freon Sludge

In previous attempts to solidify Freon sludge there was little success in obtaining solid wasteforms of greater than 10% waste by volume/5/. The extent of wasteform curing decreased as the aqueous content of the sludge increased, presumably because of the concurrently increasing detergent content of the sludge. The charge to the dry cleaning process is approximately 1% water, 1% detergent and 98% Freon 113. Since the product sludge contained over 4% water (see Table 2) the detergent content was likely close to 4% also, in addition to assorted organic, aqueous and particulate matter. The problem in this and earlier solidification tests appears to be a retarding of the cement set by detergent and emulsified organics in the sludge. These materials prevent a set by solubilizing the aluminates in the cement and forming a gel which prevents proper hydration and crystallization/9/. The Ca, OH and Cl ions are all excellent set accelerators and $CaCl_2$, in particular, will retard tricalcium aluminate hydration while facilitating hydration of the silicate phase of PC/9,10,11/. Up to 5% by weight additional calcium chloride and up to 10% by weight additional free lime have been reported as a means to utilize organic aggregates in concrete/9/. To offset retardation, calcium chloride and calcium oxide were added as set accelerators to the basic PC/imbiber bead matrix discussed earlier. The Freon sludge, like the inactive oil, was observed to be completely absorbed by the imbiber beads (oil/bead ratio of 5) in 24-48 hours. Thus the organic fraction of the sludge would be immobilized by the imbiber beads and the aqueous fraction by hydration of the cement. No emulsifier was considered necessary because of the detergent already present in the sludge waste (see Table 10).

Table 10

Wasteforms Incorporating Freon Sludge[1]

Specimen	FS2	FS12	FS4	FS5	FS8	FS10	FS26	FS30
Portland cement (PC) (g)	30	90	90	90	90	90	45	90
Limestone-injected flyash(g)	-	-	-	-	-	-	45	-
CaO (g)	-	27	25	27	-	45	27	35
$CaCl_2$ (g)	-	-	4.6	9	13.5	-	9	9
Water (mL)	33	30	30	30	30	30	30	33
Imbiber beads (mL)	6	6	6	6	6	6	8	12
Waste (mL)	30	30	30	30	30	30	40	60
Superplasticizer(% of PC)	1	1	-	2	-	5	3	4
Waste Loading (% Vol)	29	24	30	28	32	18	31	39
Compressive Strength >0.35 MPa	No[2]	No	Yes	Yes	Yes	No[3]	Yes	Yes
Organic Release (%)								
After 3d	-	<<1	<<1	<1	<1	<<1	<1	<<1
14d	-	<<1	<<1	<1	<1	<<1	<1	<1

[1] Distilled freon Waste
[2] Did not cure
[3] Wasteform dusty

In the most successful mixtures, up to 39% sludge by volume was solidified to a hard free-standing solid with a binder containing 7% $CaCl_2$, 26% CaO and the remainder Portland cement. However, despite the addition of up to 5% (by weight of cement) superplasticizer (sulphonated naphthalene formaldehyde), the resulting mixture was not very workable due to the large quantities of accelerator required. It is suggested that excess water be used and that the waste loading be reduced.

In an attempt to avoid the setting problems of PC, gypsum was tried as a binder but neither Envirostone gypsum nor plaster of Paris resulted in a hard wasteform.

The recent separation of the aqueous and Freon steps steps in the dry-cleaning process may alter either the solidification chemistry or approach and further waste characterization will be necessary.

3.5.2 Solidification of Supercompactor Effluent

The imbiber bead/Portland cement mixture was considered appropriate for supercompactor effluent because imbiber beads were needed to immobilize the organic fraction while the hydration of the PC would consume the aqueous fraction. The heterogeneous nature of the supercompactor effluent hindered the formulation of a suitable solidification mixture. Some samples such as specimen SC-11 (see Table 11) had so little organic content that no imbiber beads were required to retain the organic phase during immersion of the wasteform. When imbiber beads were used the swelling of the beads which accompanies organic phase absorption was not evident. In other samples, the variable water content of samples of the effluent was a problem. Sample SC-7 with 15 mL of acrylic mixture (mostly water) required only 30g of cement whereas SC-8 with 6 mL water and no acrylic remained wet with 30g cement.

For supercompactor effluent, 100% organic waste should be assumed and formulation E12 used. If the mixture is thin from excess water then additional cement can be used to thicken the mix. The supercompactor effluent wasteforms thus prepared were hard to the touch and released no organic material after 14 days under water.

Table 11

Wasteforms Incorporating Supercompactor Effluent

Specimen	SC2	SC3	SC5	SC7	SC8	SC11
Portland Cement (g)	100	105	90	30	30	150
Water (mL)	30	30	30	-	6	-
Imbiber beads (mL)	6	12	18	10	10	-
Waste (mL)	30	60	90	50	50	50
Epoxy (g)	-	-	-	-	8	-
Acrylic (g)	-	-	-	14	-	-
Emulsifier (mL)	0.6	-	-	-	-	-
Waste Loading (% Vol)	33	46	64	55	65	51
Compressive Strength >0.35 MPa	Yes	Yes	Yes[1]	Yes	No	Yes
Organic Release (%)						
After 3d	<<1	<<1	<<1	<1	<1	<<1
14d	<<1	<<1	<<1	<1	<1	<<1

[1] Free liquid (water) on surface after cure

3.5.3 Tritium Retention in Solidified Waste

Characterization of supercompactor effluent indicated relatively high levels of tritium (see Table 2). High levels are also expected in organic waste (eg pump oils) from the Tritium Removal Facility and much smaller amounts are found in other miscellaneous wastes. Therefore, the efficiency of specimen E12 in retaining tritiated oil was determined. Terresso 32 turbine oil was first tritiated by extended contact with tritiated moderator water and then a quantity of this tritiated oil was diluted in non-active oil and absorbed on imbiber beads over a period of 49 hours. The average activity of the oil/beads mixture (5:1 ratio) was 0.36 uCi/g. Three 5 cm right cylinder test specimens were prepared according to formulation E12 with a final waste loading of 54% oil by volume. Each test specimen was immersed in distilled water and the activity of the water was determined periodically by liquid scintillation counting of a 1 mL aliquot of the leachate. Figure 1 illustrates the tritium release rate from the wasteform.

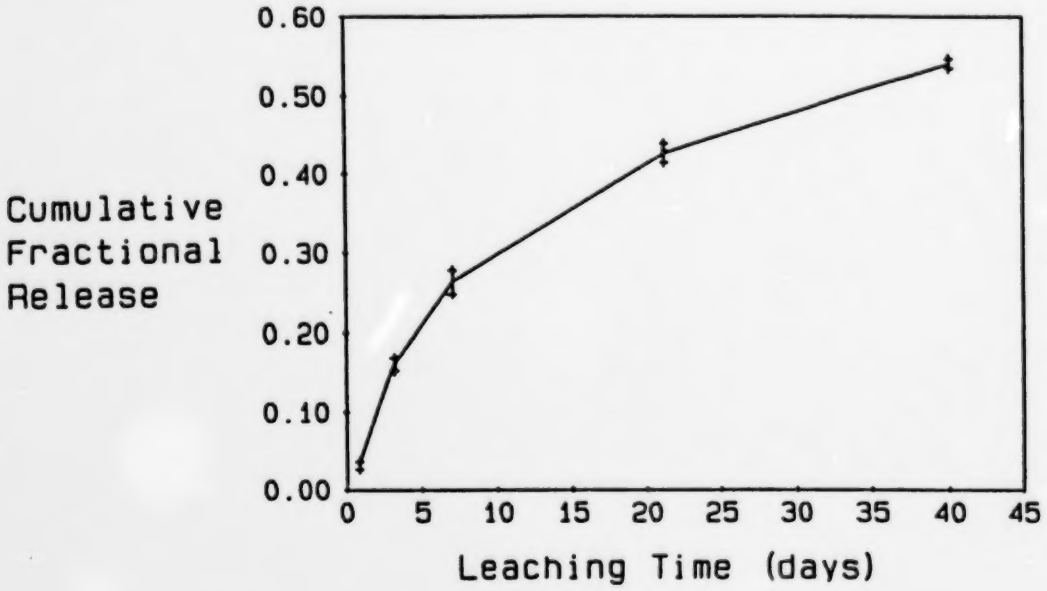

FIGURE 1: Cumulative Fractional Release of Tritium from Solidified Oil Waste.

The average initial rate of tritium release was 4% per day (see Table 12) and the average over the study period was 1.4% per day. The latter figure is probably affected by the loss of tritium in the sample and a consequent change in the concentration gradient. The rate of 4% per day (corrected for area/volume in Table 12) is greater than the release rate found for wasteforms prepared from tritiated aqueous waste/12/. It is likely that

both the relatively large oil/imbiber bead content of the waste and the larger size of the pores containing the imbiber beads provide for better mass transport of the tritium, due to greater effective porosity, when compared with the aqueous waste solid. Furthermore, any tritium incorporated in the semi-polar organic fraction of the oil would not be hindered by a hydrophilic matrix to the same extent as the tritiated water in the aqueous waste.

Table 12

Tritium Release Behaviour of Active Samples

Specimen	Solidification Medium	Initial ^{3}H Content mCi	Cumulative Fractional Release Rate (cm/day) Normalized for Area/ Volume = 1.0
E12	Portland cement/ epoxy/imbiber beads	0.02	3.3×10^{-2}
SC3	Portland cement/ imbiber beads	12.5	2.4×10^{-2}
X[1]	Portland cement	2.2 - 12.2	$1.7\text{-}2.9 \times 10^{-3}$

[1] Taken from Reference 12.

The supernatant aqueous phase recovered from immersion testing of sample SC3 indicated that 12% of the tritium in the supercompactor waste had been released over the fourteen day immersion period. When corrected for the area/volume ratio, this rate is similar to that of the E12 formulation (see Table 12). If it is assumed that the tritium resides in polar organic species, then neither retention by oleophilic imbiber beads nor exchange with hydration water will retard the release of tritium. Thus, the E12 and SC3 wasteforms, by themselves, would not be suitable solidification matrices for highly tritiated waste, but could be used in conjunction with a polyethylene container which would act as a tritium barrier. An increased transport rate of tritium through polyethylene which contains absorbed oil has been documented/12/ but the use of a solidification matrix with an oleophilic absorbent would minimize oil/polyethylene contact and interaction.

4.0 CONCLUSIONS

1. Characterization of waste oil indicates that the levels of tritium, PCB's, halogens and Fyrquel are sufficiently low for incineration.

2. Characterization of the Freon sludge and supercompactor effluent waste streams confirms that both wastes have components which could make incineration difficult. A more complete distillation of the Freon solvent in the dry cleaning waste, and absorption or dilution of the

resultant sludge with halogen-free waste could reduce halogen levels sufficiently for incineration. Management of supercompactor effluent wastes will depend on their composition. For relatively high levels of tritium, PCB's (as found in the samples analyzed here) or Fyrquel, solidification is indicated; otherwise the effluent could be absorbed on solid waste and then incinerated.

3. Supercompactor effluent and oil wastes can be solidified easily in Portland cement. Adsorbents and waterproofing agents reduce oil release when wasteforms are immersed in water. Imbiber beads and epoxy, respectively, were found to be two excellent such additives. Wasteforms prepared with these materials exhibited waste loadings of up to 60% by volume, compressive strength well in excess of 50 psi and fractional oil release on immersion for 90 days of less than 0.01.

4. Solidification of Freon sludge in Portland cement required accelerators to produce a hard wasteform. Waste loadings are generally about 20-40% with acceptable compressive strength and oil release. Mixture workability was poor due to the use of excessive accelerator addition.

5. Thermoset resins can be used in conjunction with absorbents to solidify organic liquid waste. Wasteforms produced in this way exhibit excellent compressive strength, oil retention and waste loading but the binder is relatively expensive. Wasteform performance does not justify cost when compared with modified Portland cement.

6. Waste loadings can be improved by using aqueous decontamination solution waste, of an appropriate composition and pH, in place of the cement hydration water.

7. Most of the commercially available solidification systems provided very poor oil retention. The only exception, a gelling agent (Petroset II), yielded insufficient compressive strength.

5.0 RECOMMENDATIONS

1. Waste oil should be characterized, prior to processing , to determine levels of tritium, halogens and PCBs. Low levels of these constituents, as found here, would permit incineration.

2. Supercompactor effluent and waste oil, if it must be solidified due to incinerator unavailability, transportation requirements or licensed storage requirements, should be solidified using formulation E12.

3. Further study should be conducted on Freon sludge solidification. The dry cleaning process has recently been separated into a Freon stage and an aqueous stage. Wastes from both stages should be characterized and tested for compatibility with formulation E12 or with the accelerated formulation described in Section 3.5.1 of this report.

4. Further work on absorbents needs to be conducted with the objective of finding an absorbent which does not require subsequent solidification and possesses good waste retention and waste capacity. To provide structural strength for absorbed or gelled liquid wastes, the use of rigid containers should be investigated from regulatory, storage criteria and container construction standpoints. A study of potential container materials has recently commenced/13/ at Ontario Hydro Research Division. Polycarbonate, stainless steel, fibreglass, carbon steel, HDPE are being considered initially.

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APPENDIX A

Wasteform Preparation Example (Sample E12)

1. Add 20 mL of imbiber beads to a 500 mL polyethylene jar containing 100 mL of lubricating oil. Mix together and allow to stand for 24 hours.

2. To the oil/imbiber bead mixture add 20 g epoxy while stirring (premixed Epon 815 and hardener 501). 70 g of Portland Cement Type 30 was added slowly during stirring of the above mixture with a Ceframo R2R1-64 stirrer.

3. When a homogeneous mixture was achieved, the sample was sealed and allowed to cure for 7 days prior to Phase I testing.

4. Phase II testing was conducted on samples prepared as in steps 1 and 2 and moist-cured for 28 days in 5 cm x 5 cm x 5 cm cubic molds (metal) coated with a mold release agent.

5. For samples having additives the order of component addition can be determined by selecting the appropriate steps from the following list:

    a) Waste/imbiber bead absorption
    b) Water, emulsifier, epoxy resin or acrylic suspension addition
    c) Portland cement or PC/CaO or PC/flyash or PC/gypsum binder addition
    d) Superplasticizer or calcium chloride (accelerator) addition followed by a very short final stirring period.

APPENDIX B

Origin of Materials

1. Acrylic suspension - "Acrylic Bond" U.S.E. Chemicals Ltd.
2. Sikadur epoxy - Sika Canada Inc.
3. Epon epoxy - Shell Canada Chemical Co., Toronto
4. Imbiber beads - Anco Chemicals, Mississauga, Ontario
5. Emulsifiers a) Triton X-100, X-114 - Rohm and Haas, Philadelphia, PA
   b) Solar F342 - Swift Chemical Co., Guelph, Ontario
6. Envirostone Gypsum - U.S. Gypsum Co., Chicago
7. Nutek System - Nuclear Technology Corporation, Anston, Conn.
8. Petroset II - Fluid Teck, Las Vegas, Nevada

APPENDIX C

Decontamination Solution Characteristics

Name	Composition	Concentration of Use g/kg	pH of Use
Turco 4521A	ammonium citrate 66% oxalic acid 34%	50	4.0
Calgon	sodium hexametaphosphate	10	7.5
Nacconal	detergent	10	7.8
Pickering Solution	sodium hexametaphosphate 50% detergent 25% EDTA 25%	10	6.5
STPP	sodium tripolyphosphate	10	9.0
Peroxide Bicarbonate	sodium carbonate 57% sodium bicarbonate 27% hydrogen peroxide 16%	127	9.8
Alkaline Permanganate	sodium hydroxide 77% potassium permanganate 23%	130	13.0